



# Analysis of the solid electrolyte interphase formed with an ionic liquid electrolyte for lithium-sulfur batteries



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## HIGHLIGHTS

- A stable SEI on lithium electrodes is formed with ionic liquid electrolyte.
- Presence of polysulfides results in a higher resistance for Li-ion transfer across the SEI.
- Presence of polysulfides results in a SEI film with different chemical composition.

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## ABSTRACT

We have investigated the formation of the solid electrolyte interphase (SEI) on lithium electrodes in the presence of an ionic liquid electrolyte with a particular focus on the influence of polysulfides present in the electrolyte on the SEI. The electrochemical performance of symmetric cells with lithium electrodes and electrolytes composed of *N*-Methyl-(*n*-butyl)pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR14-TFSI) and LiTFSI, with and without the addition of polysulfides, were analyzed as well as the chemical composition of the SEI, before and after cycling. The cycling behavior of the symmetrical cells shows that the SEI films are relatively stable in the ionic liquid electrolyte, also in the presence of polysulfides. However, the presence of polysulfides results in a higher SEI layer resistance ( $R_{SEI}$ ) and a higher activation energy. From X-ray photoelectron spectroscopy spectra (XPS), with argon-ion sputtering for depth profiling, we find that the SEI is formed by decomposition products from both cations and anions of the electrolyte. The XPS spectra show that the presence of polysulfides alters the decomposition process of the electrolyte, resulting in a SEI film with different chemical composition and structure, in line with the results from the electrochemical performance.

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## 1. Introduction

High-performance lithium batteries are becoming more and more critical to satisfy the increasing performance demands of communication and portable electronic devices and electric and hybrid vehicles [1–3]. However, the overall energy density of current lithium ion batteries is not enough for key applications of the future [4,5]. Thus, large efforts are devoted to develop a new generation of battery systems with higher energy density [4,6]. Among the different possible technologies lithium-sulfur batteries are among the most promising candidates due to their high theoretical energy density (about 2600 Wh kg<sup>−1</sup>), natural abundance of key elements and environmental friendliness [6–13]. However, the

lithium-sulfur battery concepts so far suffer from several drawbacks, such as capacity degradation upon cycling, low utilization of active materials, and low coulombic efficiency [14–18]. In literature, different strategies are considered to improve the performance, including the optimization of the electrolyte composition [19–23]. Due to their low viscosity and high solubility of polysulfides, ether-based electrolytes are most commonly used in lithium-sulfur batteries [19,24–27]. However, these organic solvents reduce the safety of the battery because of their low flash point and flammability [19,20,28,29].

The introduction of room temperature ionic liquids (RTILs) based electrolytes is an effective strategy to overcome the safety issue, owing to their wide electrochemical window, high thermal stability, and nonflammability [30–33]. During the last few years, there have been several attempts to develop lithium-sulfur batteries with RTILs based electrolytes. *N*-Methyl-(*n*-butyl)pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR14-TFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

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(EMIm-TFSI) have been investigated as base for lithium battery electrolytes [34,35]. Shin et al. [36,37] have employed poly(ethylene glycol)dimethyl ether (PEGDME) and tetra(ethylene glycol)dimethyl ether (TEGDME) as a polymer solvent in mixed electrolytes composed of PYR14TFSI, the Li-salt LiTFSI, and the solvents. Furthermore, they characterized the electrochemical properties of lithium-sulfur batteries with this mixed electrolyte. Recently, a lithium-sulfur battery with prelithiated Si/C anode and an ionic liquid electrolyte was reported by Yan et al. [38]. In the previous reports, the behavior of the lithium anode has received little attention although lithium anode also plays a key role to overcome the challenges of lithium-sulfur batteries.

The electrochemical behavior of lithium electrodes in RTIL based electrolytes has been discussed in previous publications [39–41]. However, the effect of reaction intermediates (polysulfides) on the lithium electrode should also be considered in lithium-sulfur batteries since they are soluble in the electrolyte [42]. The presence of polysulfides in the electrolyte can dramatically affect the formation of the solid electrolyte interphase (SEI) which dominates the electrochemical behavior of the lithium anode [43–48]. Recently the formation of the SEI on the lithium electrode in a lithium sulfur battery using ionic liquid as a co-solvent was investigated [41]. As substantially higher interphase resistance was found in the case of the ionic liquid present in the electrolyte, along with organic solvents, closely related to a change in the chemical composition of the SEI-layer.

In this work we focus on the development of the SEI on the lithium electrode in the presence of a pure ionic liquid electrolyte (PYR14-TFSI/LiTFSI) with the aim to disentangle to effect of the presence of polysulfides in the electrolyte solution on the SEI formation. The formation of the SEI and its chemical composition was analyzed using electrochemical measurement and X-ray photoelectron spectroscopy (XPS), including a depth profiling of the SEI layer. The results show that a stable SEI film is obtained in RTIL based electrolytes, both with and without polysulfides present. However, the presence of polysulfides results in a change in the resistance related to the charge transfer across the interface between the SEI film and the lithium electrode. The XPS results provide evidence that the presence of polysulfides in the electrolyte modifies the chemical composition and structure of the SEI film. This result is of importance when considering ionic liquid based electrolytes for lithium-sulfur batteries where polysulfides play a key role in the electrochemical process [12,49].

## 2. Experimental

Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 99.95%, Sigma–Aldrich), *N*-Methyl-(*n*-butyl)pyrrolidinium bis(trifluoromethylsulfonyl)imide (PYR14-TFSI, 99.9%, Solvionic, water content 20 ppm analyzed by Karl Fischer titration), sulfur (reagent grade, Sigma–Aldrich) and lithium sulfide (99%, Sigma–Aldrich) were used to prepare ionic liquid electrolytes with and without polysulfides. All materials were stored in a glove box ( $H_2O < 1$  ppm,  $O_2 < 1$  ppm) under argon atmosphere before sample preparation. The mixture of LiTFSI and PYR14-TFSI (LiTFSI concentration,  $0.4 \text{ mol kg}^{-1}$ ) was stirred to prepare the RTIL electrolyte (400 rpm for 24 h). For the electrolyte with polysulfides, sulfur powder and lithium sulfide (7:1, mol/mol) were added to the ionic liquid (PYR14-TFSI) and stirred under the same condition. Subsequently, LiTFSI was added at the same molality ( $0.4 \text{ mol kg}^{-1}$ ) and stirred for another 24 h. The ionic conductivity of the electrolytes was measured from  $5^\circ\text{C}$  to  $40^\circ\text{C}$  in a gold-plated cell with  $100 \mu\text{m}$  glass fiber spacers, in the frequency range  $0.01 \text{ Hz} - 1 \text{ MHz}$  using a Novocontrol broadband dielectric spectrometer.

Lithium metal foil ( $200 \mu\text{m}$ , Chemetall Foote Corp.) was cut into  $10 \text{ mm}$  diameter disks as lithium electrodes. Two lithium disks,

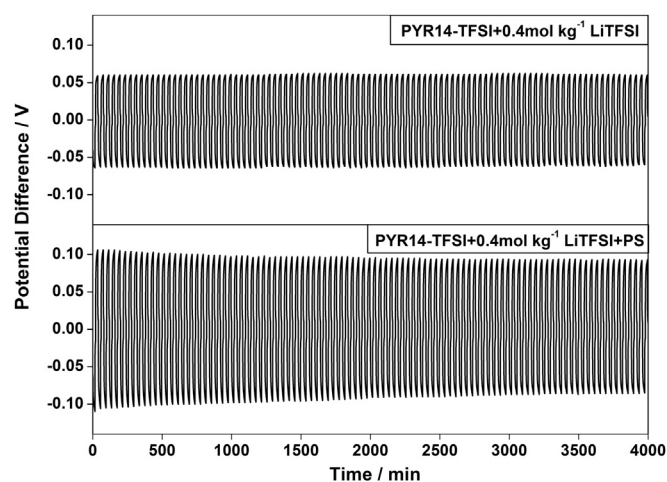


Fig. 1. Cycling behavior of symmetrical cells with the two different electrolytes ( $40^\circ\text{C}$ ,  $0.1 \text{ mA cm}^{-2}$ ).

separator ( $20 \mu\text{m}$ , Celgard® 2400) and electrolytes were assembled to symmetrical coin cells. The cycling performance of the symmetrical cells was tested using a multi-channel electrochemical analyzer (Ivium-n-Stat instrument, Ivium Technologies B.V.) at a current density of  $0.1 \text{ mA cm}^{-2}$  (15 min charge, 15 min discharge and 5 min open circuit in each cycle). Impedance spectroscopy measurements were performed on a Novocontrol broadband dielectric spectrometer from  $5^\circ\text{C}$  to  $40^\circ\text{C}$ , over a frequency range of  $1 \text{ MHz}$  to  $0.01 \text{ Hz}$  and the perturbation amplitude was  $5 \text{ mV}$ .

After cycling the cells were disassembled carefully to retrieve the lithium electrodes for further characterization of the SEI with XPS. The lithium electrodes were washed with dimethyl carbonate (DMC) twice, 1 min for each washing. After washing, the lithium electrodes were left to dry under vacuum for 30 min to remove any residual DMC. All operations were carried out inside the glove box. An argon atmosphere controlled glove bag (Aldrich) was employed to transfer the electrodes from the glove box to the XPS systems (PHI 5800, Physical Electronics). XPS analysis was performed with Al-K $\alpha$  radiation ( $200 \text{ W}$ ,  $13 \text{ kV}$ ) as X-ray source at a pressure of  $10^{-9}$  Torr. The diameter of the analyzed area was  $800 \mu\text{m}$ . An argon ion beam (accelerating voltage  $3 \text{ kV}$ , emission current  $10 \text{ mA}$ ) was employed to perform depth profiling (etching area,  $1 \text{ mm} \times 1 \text{ mm}$ ).

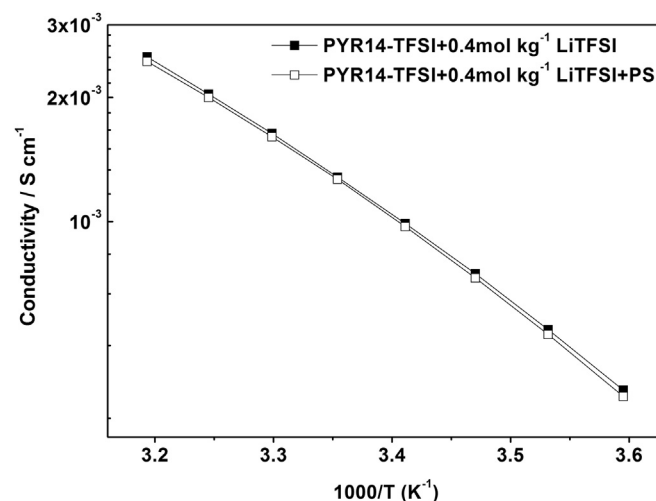


Fig. 2. Ionic conductivity as a function of temperature for the PYR14-TFSI based electrolyte with and without addition of polysulfides.

### 3. Results and discussion

Fig. 1 shows the cycling behavior of the symmetric cells with the ionic liquid based electrolytes (with and without polysulfides). The level of changes of the potential under a constant current is a good indication of the stability and resistance of a system during cycling [40]. As shown in Fig. 1, the potential of the symmetrical cell with the PYR14-TFSI based electrolyte maintains a stable level over the whole period of cycling. This suggests that the SEI film on the lithium electrode, formed from the PYR14-TFSI based electrolyte, is relatively stable over repeated cycles. With the addition of polysulfides the potential slowly decreases over the first dozens of cycles and then reaches a stable level with further cycling. This reveals that the presence of polysulfides leads to some change in the formation and stability of the SEI film. Furthermore, the potential of the cell is higher in this case, even though the conductivity of the two electrolytes is quite similar, as shown in Fig. 2. Thus, the higher potential is a result of a higher resistance for lithium ions of the SEI film in the presence of polysulfides, increasing the polarization at the interface and leading to the higher potential observed under a constant current.

Figs. 3 and 4 show impedance spectra and Arrhenius plots of the SEI resistance obtained from the symmetrical cells, with and without polysulfides, before cycling and after different numbers of cycles. As seen in Fig. 3 (a), the spectra of the cell with the PYR14-TFSI based electrolyte show only one semicircle, both before and

after cycling. This is characteristic of a situation where the resistance for the transfer of Li-ion across the SEI film ( $R_{SEI}$ ) contributes to the main part of the spectra [50,51]. Furthermore, the resistance of the SEI film formed in PYR14-TFSI based electrolyte is higher than that for the native film on the lithium electrode before cycling. After cycling, there are no major changes of the resistance of the SEI film, which indicates that the film formed on the electrode is rather stable during cycling. In contrast, the spectra of the cell cycled with the electrolyte containing polysulfides (Fig. 4(a)) show two semicircles corresponding to the resistances for the transfer of Li-ion across the SEI film ( $R_{SEI}$ ) and the charge transfer across the interface ( $R_{ct}$ ) respectively [52,53]. This shows that the presence of polysulfides leads to a SEI film with different transfer properties. The  $R_{SEI}$  of the film formed with polysulfides is rather stable during cycling, while the  $R_{ct}$  decreasing with cycling.

Fig. 5 shows the resistance for Li-ion transfer across the SEI film ( $R_{SEI}$ ) and the activation energy ( $E_a$ ) as a function of the cycle number for the two cells, with and without polysulfides. The  $R_{SEI}$  for the cell cycling with polysulfides is higher than the one without whether before or after cycling. However, one can note that  $R_{SEI}$  for both cells are one order of magnitude higher than for cells with an organic solvent based electrolyte [47,49,54], and in good agreement with the results reported for Li-sulfur battery containing an ionic liquid electrolyte [41]. From the temperature dependence of the resistance for the transfer of Li-ion across the SEI film we can also determine the activation energy for this process  $1/R_{SEI} = A \exp(-E_a/$

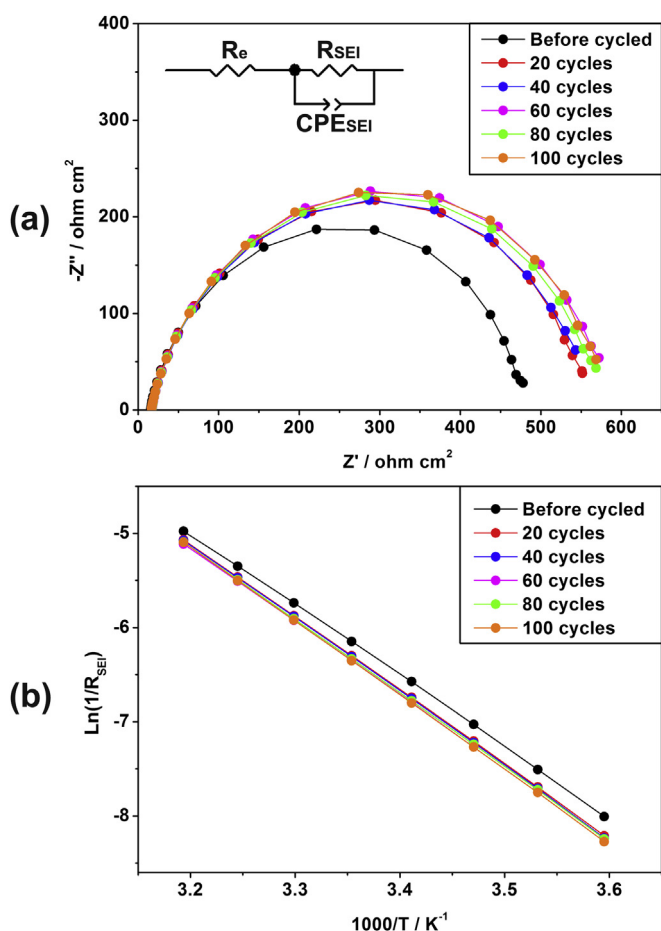


Fig. 3. (a) Impedance spectra (25 °C) from the symmetrical cell with the PYR14-TFSI + 0.4 mol kg<sup>-1</sup> LiTFSI electrolyte after different numbers of cycles. Inset shows the equivalent circuit used to analyze the spectra (b) Arrhenius plot of SEI resistance.

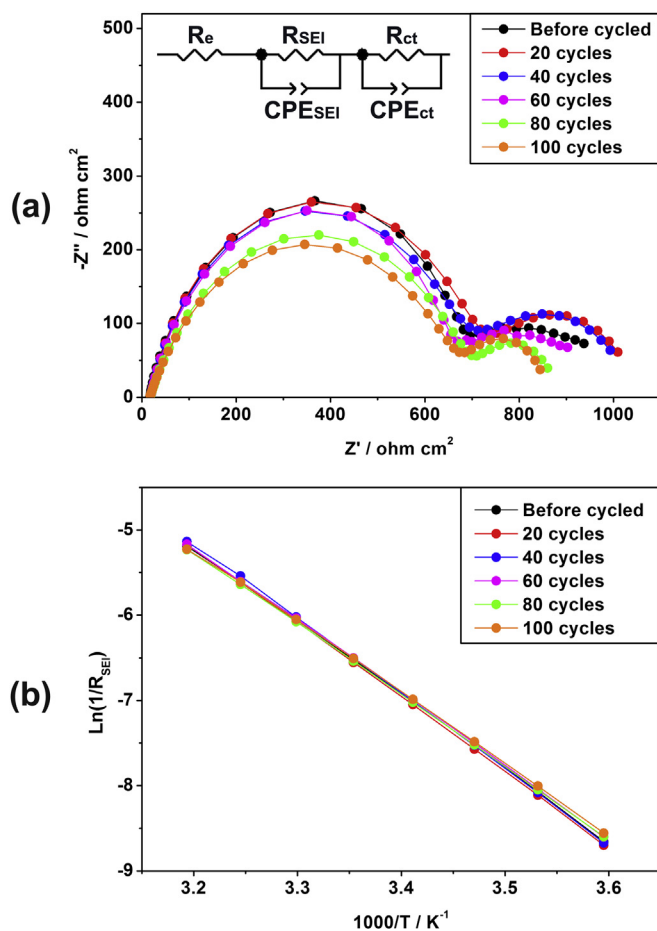


Fig. 4. (a) Impedance spectra (25 °C) from the symmetrical cell with the PYR14-TFSI + 0.4 mol kg<sup>-1</sup> LiTFSI + polysulfides electrolyte after different numbers of cycles. Inset shows the equivalent circuit used to analyze the spectra (b) Arrhenius plot of SEI resistance.

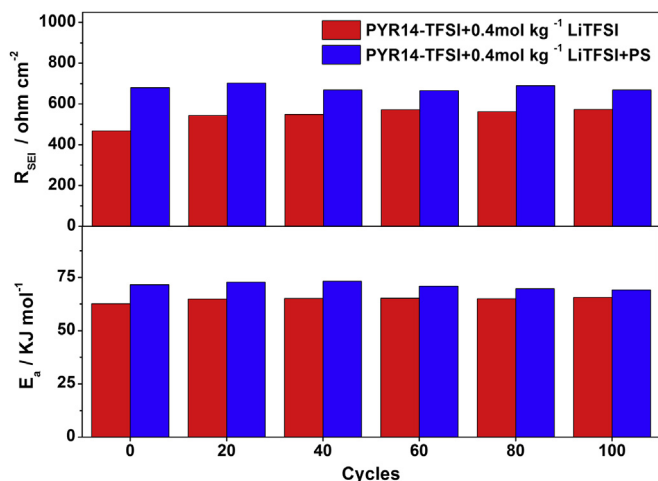


Fig. 5.  $R_{SEI}$  (25 °C) and activation energy as a function of the cycle number for the cells cycling in different electrolytes (PS, polysulfides).

RT), where  $A$ ,  $E_a$ ,  $R$ , and  $T$  denote the pre-factor, activation energy, gas constant, and temperature, respectively [50,55]. The values obtained for the activation energy is in good agreement with results previously reported for conventional electrolytes, other ionic liquids and for other Li-salts [50,55,56]. There are no major changes of the activation energy in the SEI films formed with and without polysulfides during cycling. However, the activation energy for the SEI film with polysulfides is always higher [57].

The difference in the electrochemical performance between the two SEI films can be attributed to differences in the decomposition of the electrolyte on the lithium electrode, resulting in different chemical composition of those films. From the XPS experiment, with depth profiling, we obtain information about the chemical composition of the SEI film formed on the electrode. Fig. 6 shows the XPS spectra in the C1s, F1s, and S2p regions for different sputtering times. As shown in Fig. 6a, the C1s spectra of the electrode cycled with the ionic liquid electrolyte without polysulfides indicate the presence of species associated with C–H around 284.0 eV, C–N at 286.1 eV, and  $-\text{CF}_3$  at 291.0 eV [55,58,59]. In the F1s spectra the signature of  $-\text{CF}_3$ , at 688.9 eV, is found

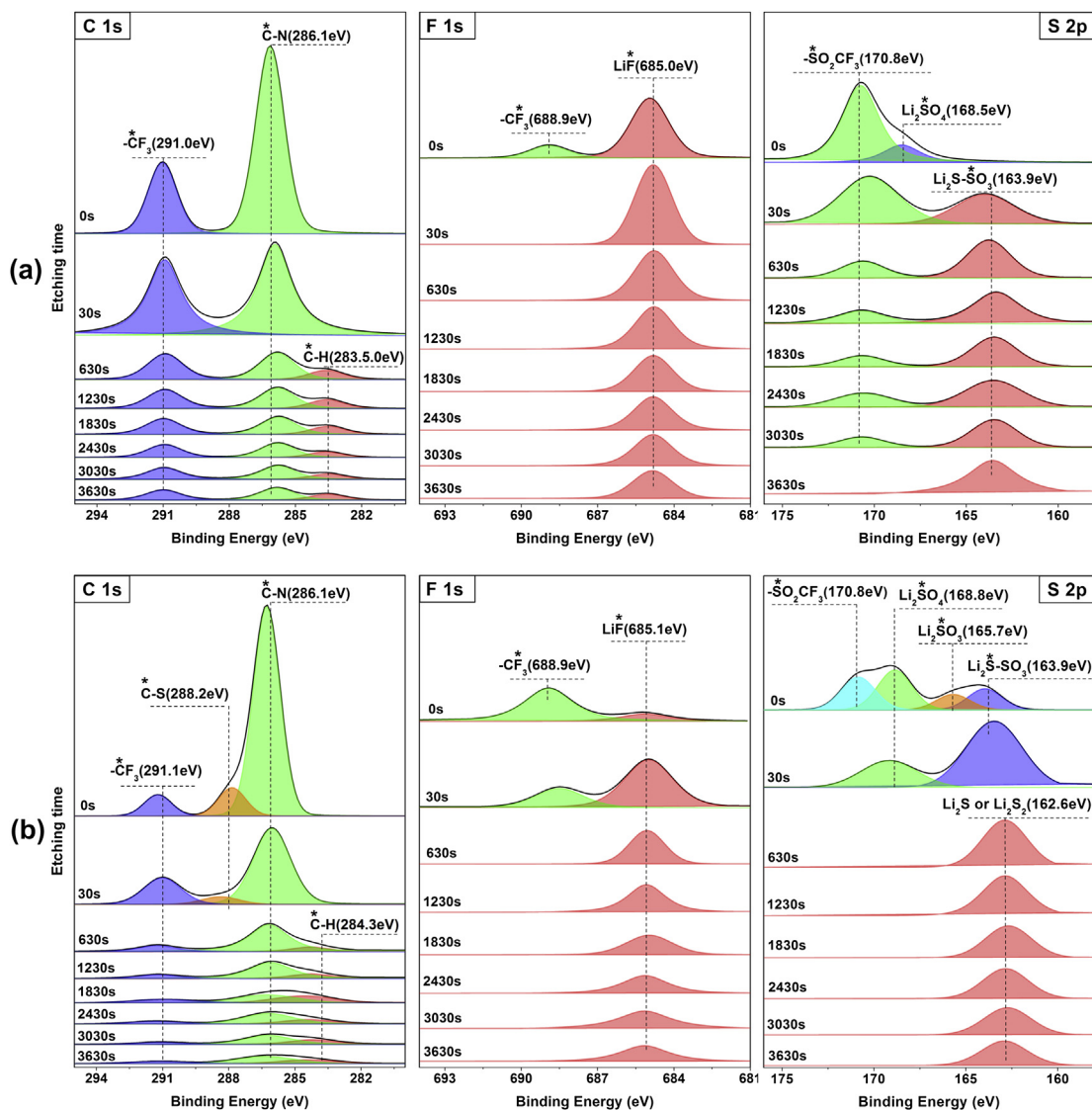
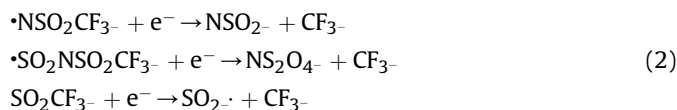
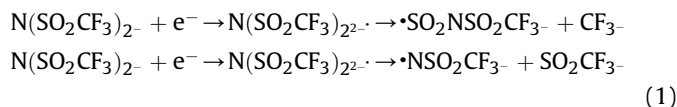


Fig. 6. X-ray photoelectron spectroscopy (XPS) spectra from lithium electrodes cycled in (a) PYR14-TFSI + 0.4 mol kg<sup>-1</sup> LiTFSI and (b) PYR14-TFSI + 0.4 mol kg<sup>-1</sup> LiTFSI + polysulfides for 100 cycles.



together with a peak at 685.0 eV corresponding to LiF [55]. In the S2p spectra the peaks can be associated to  $-\text{SO}_2\text{CF}_3$  species at 170.8 eV,  $\text{Li}_2\text{SO}_4$  species at 168.5 eV and  $\text{Li}_2\text{S}-\text{SO}_3$  at 163.9 eV [49,55,59,60]. The distribution of species is rather homogeneous as a function of sputtering time even though the relative amount of C–H increases as a function of sputtering. These results indicated that the main contribution to the SEI-film formed on the anode comes from the decomposition of the TFSI anion, shown by the large presence of S and F compounds, even though some decomposition products of the PYR14 cation, as indicated by the  $-\text{CH}$  and  $-\text{CN}$  components, most likely also contribute to the film formation. Previous publications have suggested that the decomposition of the TFSI anion in RTILs can be summarized to two main steps [61,62]:



Considering the composition of the SEI film on the Li-electrodes our results are in agreement with these decomposition steps.

A significant difference is found when the results for the electrodes cycled with and without polysulfides in the electrolyte are compared, Fig. 6a–b. The C1s spectra from the SEI film formed with polysulfides show the presence of C–S species at 288.2 eV and less species with  $-\text{CF}_3$  [55], in the F1s spectra there is much less contribution from LiF in the surface layer, and in the S2p spectra the ratio between the  $-\text{SO}_2\text{CF}_3$ ,  $\text{Li}_2\text{SO}_4$  and  $\text{Li}_2\text{S}-\text{SO}_3$  peaks has changed and further down in the layer an indication of lithium sulfides species at 162.6 eV is found [49,59]. This clearly shows that the chemical composition of the SEI-film formed in the presence of polysulfides is different from the one formed in the ionic liquid electrolyte without polysulfides. The difference in composition suggests that there might be difference in the decomposition process of the electrolyte on lithium electrodes due to the polysulfides in the electrolyte, but one can also envision the direct incorporation of polysulfides into the SEI.

The difference between the structure of the two SEI films is further confirmed by the depth profile, as shown in Fig. 7. In the surface layer of the SEI film formed in the PYR14-TFSI based electrolyte, compounds with F account for the majority of the decomposition products from TFSI anions. In the presence of polysulfides, compounds with F and S account for the majority. With increasing depth, the concentration for N, S and F decrease to a very low level after 1230s etching and the chemical composition for SEI films are dominated by Li, C and O, which can be attributed to the lithium metal and residual native film consisting of  $\text{Li}_2\text{O}$  [48,59].

From our results we find that there is a direct correlation between the electrochemical properties and the composition of the SEI-film on the lithium electrode. Compared with SEI films formed in a conventional electrolyte [41] the resistance is higher when an ionic liquid electrolyte is used but also the composition of the film is different, in particular the sulfur containing species are different. The surface of our film is dominated by  $-\text{SO}_2\text{CF}_3$  species whereas in the case of an organic solvent  $-\text{SO}_2/\text{SO}_3$  species dominate [41]. Furthermore one can expect a considerable contribution also from the breakdown of the organic solvent molecules in the SEI formed in an organic solvent whereas the main contribution in the SEI formed in our work is attributed to the breakdown of the TFSI<sup>−</sup>

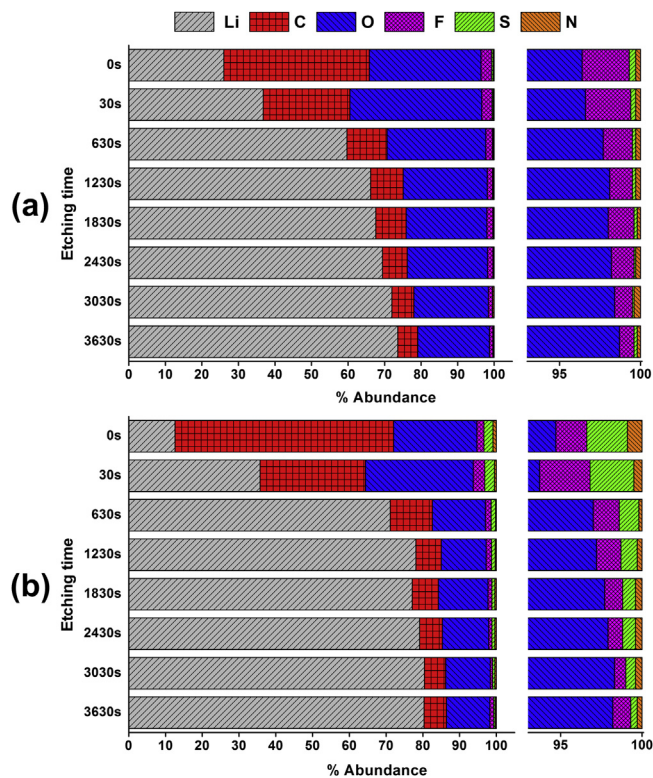


Fig. 7. Depth profile for the lithium anode surface cycling in (a) PYR14-TFSI + 0.4 mol kg<sup>−1</sup> LiTFSI and (b) PYR14-TFSI + 0.4 mol kg<sup>−1</sup> LiTFSI + polysulfides. Right column: A close up for F, S and N.

anion. With the addition of polysulfides to the electrolyte we see a further modification of the chemical composition of the SEI, by the incorporation of different sulfide species in particular in the surface layer, which can be correlated with the further increase in the interfacial resistance and in the activation energy. The fact that the addition of polysulfides mainly influences the surface layer can be connected to the slightly lower stability of the SEI as revealed from the impedance measurements.

#### 4. Conclusions

To understand the effect of polysulfides on the SEI formation and the behavior of lithium electrodes during cycling in RTILs based electrolytes, the electrochemical performance and structure of the SEI film formed in electrolytes composed of PYR14-TFSI, polysulfides and LiTFSI were analyzed using electrochemical measurement and X-ray photoelectron spectroscopy. The presence of polysulfides in the electrolyte is a characteristic in lithium-sulfur batteries and thus their influence on film formation on the anode is a key issue. A stable SEI film is formed in RTILs based electrolytes whether with or without polysulfides. The SEI layer resistance and the activation energy for the cell cycling with polysulfides are higher than the one without, both before and after cycling. Furthermore, the presence of polysulfides results in an additional resistance at medium frequency. The XPS spectra with depth profiling indicate that decomposition of the RTILs based electrolyte, mainly the anion, occurs during cycling, with and without polysulfides. However, the chemical composition of the SEI-film is different in the presence of polysulfides, containing more sulphide related species in the top layer. This difference can be directly linked to the difference in the electrochemical behavior of lithium electrodes cycling in different electrolytes.

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